

Chapter I

The general problem of the stability of microstructure

I.1 Introduction

Materials science in general and metallurgy in particular are concerned with understanding both the structure of useful materials, and also the relationship between that structure and the properties of the material. On the basis of this understanding, together with a large element of empirical development, considerable improvements in useful properties have been achieved, mainly by changes in the microstructure of the material. The term *microstructure* as normally used covers structural features in the size range from atoms (0.3 nm) up to the external shape of the specimen at a size of millimetres or metres. These structural features include the composition, the crystal structure, the grain size, the size and distribution of additional phases and so on, all of which are controlled by the normal methods of alloying, fabrication and heat treatment.

The materials scientist, having achieved some sort of optimum microstructure for a particular property or application, has not completed the task. The important area of the *stability* of the microstructure remains to be considered. This concern arises since almost none of the useful structures in materials science are *thermodynamically* stable: changes that will increase the total entropy or decrease the material's free energy are almost always possible. So if the original structure was an optimum one then such changes will degrade the material's structure and properties. This idea of inherent instability, particularly of metallic materials, is widely appreciated in the context of corrosion, where a metal, having been won from its ore, continually attempts to return to a chemically more stable form, normally that of an oxide. Although a discussion of corrosion

does not concern us here, the characteristic that allows a metal to remain a metal is the same as that which maintains unstable microstructures – the *slow kinetics* of the degradation. The rates of structural and chemical change must be sufficiently slow to allow the material a useful lifetime.

In subsequent chapters of this book we shall look at the stability of metallic microstructure with respect to the various examples of thermodynamic instability. In each example, the form and amount of potential free energy decrease will be established first, then the mechanisms by which the decrease of free energy can occur will be examined and finally, using these ideas, the current experimental and theoretical understanding of the *kinetics* of the structural change will be discussed. It is not usually profitable to divide microstructural transformations into separate classes – those giving desirable microstructures and those in which desirable microstructures degrade. An obvious illustration of this is the process of grain growth (§5.8). For strength and toughness at room temperature a small grain size is usually needed. However, at temperatures above about half of the absolute melting temperature ($0.5T_m$), deformation by grain boundary sliding and diffusion creep makes a fine-grain-sized material weaker than the same material with a large grain size. As a consequence of the difficulty of determining which changes are desirable and which not, we shall discuss the structural changes irrespective of their desirability from an engineering standpoint. The distinction between different types of transformation will be made solely on the basis of the type of thermodynamic driving force involved in the transformation.

There are two different types of structural instability, the first of which is a genuine *instability* and the second is normally described as showing *metastability*. In the case of metastability, before a system can achieve the more stable state with lower energy, it must pass through an intermediate transition state having *higher* energy. This requirement of passage through a higher energy state then acts as a barrier to the transformation. Unless the necessary *activation energy* can be supplied to the system the reaction cannot take place and the system will spend extended times in the initial metastable state. For an instability, however, no such barrier exists. A clear mechanical analogy has been provided by Cahn (1968) and is shown in fig. 1.1. Here the metastable situation is provided by a rectangular block balanced on its narrow end while the unstable situation is a wedge balanced on its end.

The distinction between metastable and unstable structural transformations in materials was first made by Gibbs (1878), the founder of the subject. In a Gibbs Type I transformation, the energy barrier exists in the need to nucleate a critical-sized nucleus of the new structure before the lower energy transformed structure can grow. This process is usually described as one of *nucleation and growth*. It involves a transformation described as being large in the magnitude of the structural change but localised in a small part of the sample. That is, the partially trans-

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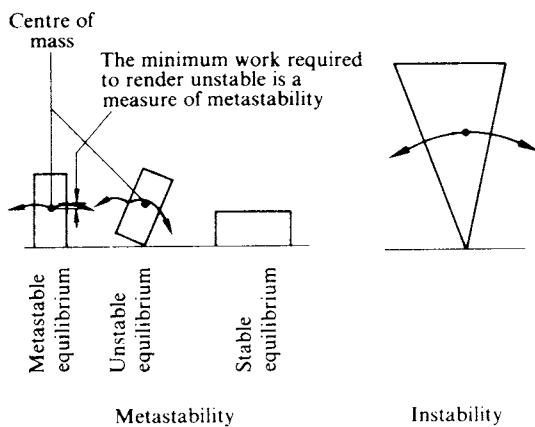


Figure 1.1 Difference between metastability and instability. (After Cahn 1968, courtesy of AIME.)

formed structure is *heterogeneous* with small regions of the new structure embedded in the untransformed initial structure. The energy barrier to this type of transformation arises mainly from the energy of the interface between the two different structures. In the alternative mode of transformation, Gibbs Type II, the unstable structure is able to transform into the more stable form by passing through a continuous series of intermediate stages, each of which has a steadily reducing energy. Gibbs Type II transformations are ones that, at least initially, have a structural change that is small in magnitude but is unlocalised – that is, there is a small change in structure but one taking place *homogeneously* throughout the sample. The best-known example of this type of transformation is that provided by the ‘spinodal decomposition’ of a solid solution (§2.2.1). In spinodal decomposition a supersaturated solution decomposes into two phases with different compositions but each having the same crystal structure and orientation.

Gibbs’ distinction between metastable and unstable transformations is well established. It should be noted, however, that both types of transformation involve atomic mobility and for this mobility thermal activation is necessary to overcome the energy barrier to move an atom from one site to another. As a result, the real distinction between the two types of change becomes that in a metastable change *many* atoms are involved in the activation step while in unstable changes only single atom activation is necessary. As a consequence, in none of the changes discussed in this book is the *inertia* of atoms a significant factor in the kinetics of the change. The necessity of providing thermal atomic activation means that at temperatures low compared with the absolute melting point, most of the changes discussed here will occur at a negligible rate. Significant rates of change will occur only at temperatures somewhat greater than about $0.3T_m$. For changes requiring atomic movement over more than a few atomic spacings the temperature for the onset of a significant rate of reaction is normally $0.5T_m$. That is, the instabilities do not concern most metals used at room temperature. Low melting point lead alloys are, however, exceptions to this restriction.

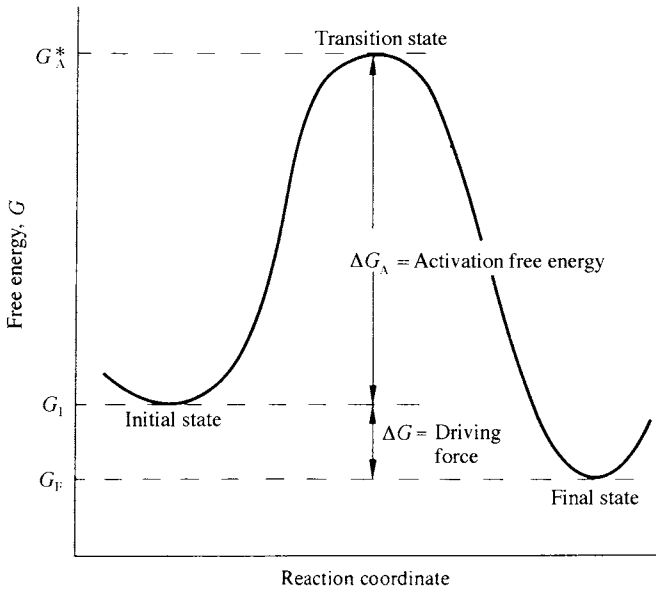


Figure 1.2 The change in free energy of an atom as it takes part in a transition. The 'reaction coordinate' is any variable defining the progress along the reaction path.

The parameter driving all solid state structural transformations at constant temperature, T , and pressure, P , is the reduction of Gibbs free energy, G of the material:

$$G = H - TS = U + PV - TS \quad (1.1)$$

Here H is the enthalpy, S the entropy, U the internal energy and V the volume of the material. The alternative form of free energy is the Helmholtz free energy, F , eq. (1.2), which seeks a minimum value for reactions at constant temperature and constant volume:

$$F = U - TS \quad (1.2)$$

Since constant pressure, at 1 atm, is the usual condition that most engineering materials experience we shall use the Gibbs free energy, G , which we will for the rest of this volume refer to merely as the free energy. In chapter 5, some consideration is given of microstructural changes that can take place in a *temperature gradient* so then it is incorrect to use the condition of a minimisation of G . The thermodynamic parameter that must be used is the maximisation of total entropy. The total entropy includes both the entropy change of the material and the entropy changes of the surroundings. The value of using the concept of free

energy minimisation, at constant temperature, is that we need only consider changes in the material and can ignore changes in the surroundings.

The change in free energy of an atom as it takes part in a transition may be represented by fig. 1.2, in which the ‘reaction coordinate’ is any variable defining the progress along the reaction path. G_I is the mean free energy of an atom in the initial configuration and G_F is that after transformation. $\Delta G = (G_F - G_I)$ is negative and provides the driving ‘force’ for the transformation. The movement of the atom from the initial state to the final state is opposed by the free energy barrier ΔG_A , so until the atom can temporarily acquire the necessary extra energy to carry it over this barrier, it will remain in the initial (metastable) state. The smallest energy increment (ΔG_A) which will allow the atom to go over the barrier is the *activation free energy* of the reaction. An atom having the maximum free energy, G_A^* , in the ‘transition’ or ‘activated’ state is unstable and will either fall forward into the transformed state or back into the initial state.

The additional free energy needed for the atom to undergo the transformation is supplied by thermal energy, so it is to be expected that the reaction velocities will depend upon the magnitude of ΔG_A and upon the form of the energy distribution resulting from random thermal motion. In most problems of practical interest ΔG_A is much greater than the average thermal energy kT , so the rate of surmounting the energy barrier is then very small and an atom held up by the barrier spends most of its time near G_I .

By treating the activated state as a quasi-equilibrium state, with the number of particles per unit volume in the transition state C_A and in the initial state C_I , then, assuming equilibrium exists between the two configurations, an equilibrium constant, K^* , may be written as:

$$K^* = C_A / C_I \quad (1.3)$$

K^* is given by the thermodynamic relation:

$$K^* = \exp(-\Delta G_A / kT) \quad (1.4)$$

Since the rate of transformation will be proportional to C_A we can write the rate as given by:

$$\text{Rate} = \text{constant} \cdot C_I \cdot \exp(-\Delta G_A / kT) \quad (1.5)$$

The constant in eq. (1.5) involves the vibration frequency ν (s^{-1}) of atoms in the activated state. This frequency is usually approximated as the atomic vibration frequency of atoms in the initial state.

It is often more convenient to discuss the thermodynamics in terms of an enthalpy of activation ΔH_A and an entropy of activation ΔS_A which are related to

ΔG_A by the standard equation:

$$\Delta G_A = \Delta H_A - T\Delta S_A \quad (1.1a)$$

Eq. (1.5) may then be written:

$$\text{rate} = A \exp(-\Delta H_A/kT) \quad (1.6)$$

That is, the entropy component, ΔS_A , is included within the pre-exponential frequency factor, A . Eq. (1.6) is the well-known Arrhenius equation and applies to many problems in atomic kinetics. To fit it to experimental observations it is written in the logarithmic form:

$$\ln \text{rate} = \text{constant} - \Delta H_A/kT \quad (1.7)$$

Eq. (1.7) shows that the logarithm of the rate of change should vary linearly with the reciprocal of the absolute temperature. A vast number of physical and chemical reactions, both homogeneous and heterogeneous, behave in this way, indicating that the standard Arrhenius model for the thermally activated reaction rate is valid.

The great effect of temperature on reaction rates is due to the exponential energy factor. Taking a typical value for metallurgical processes, for example, of ΔH_A of 2 eV per atom, with Boltzmann's constant k of 8.6×10^{-5} eV K⁻¹, we obtain at 1000 K, $\exp(-\Delta H_A/kT) = 10^{-10}$, and at 300 K, $\exp(-\Delta H_A/kT) = 10^{-33}$. This implies that a reaction taking 1 s at 1000 K will take about 3×10^{14} y at room temperature. Such changes in rates are the basis of the usual heat-treatment processes to produce structures that, after cooling, are metastable at room temperature for very long times. The larger the value of ΔH_A , the more rapid is the variation of reaction rate with temperature, and the easier it becomes to preserve by quenching to room temperature a structure which exists in equilibrium at high temperature but which would decompose during slow equilibrium cooling.

1.2 Driving forces for microstructural change – reduction of free energy

The term driving 'force' is not formally appropriate for these changes since the free energy is usually not a simple function of distance, and so the idea of a force, the differential of free energy with respect to distance, is not really appropriate. However, in the qualitative sense of causing the transformation we think of the magnitude of the free energy changes as indicating the relative 'driving forces' for the different changes to be discussed. In addition, many changes are driven

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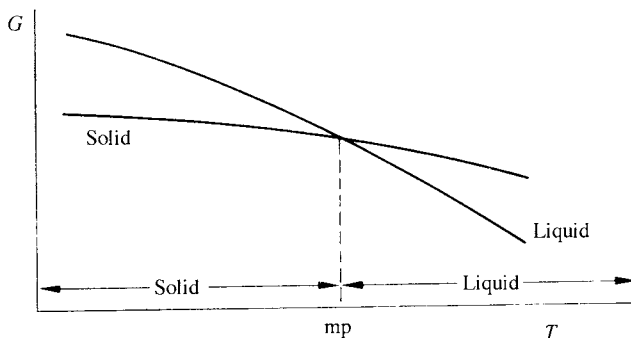


Figure 1.3 Variation of free energy with temperature for a pure metal.

by a constant free energy change *per unit volume* in units of J m^{-3} , and for all such changes there is a constant pressure, a force per unit area of interface at the interface between parent and daughter phases. This pressure has the same magnitude as the free energy per unit volume but its units are N m^{-2} .

The driving forces for the changes to be discussed in chapters 2, 4 and 5 are the changes in *chemical*, *strain* and *interfacial* free energies respectively. What is meant by chemical free energy is the free energy of strain-free regions of a phase, by strain energy is the increase of free energy caused by short and long range elastic strains, and by interfacial free energy the extra free energy of atoms at interfaces between phases and at grain boundaries. There cannot be a complete distinction between these concepts since, for example, the chemical free energy of a non-uniform solute distribution (§2.1) will have a strain energy contribution if the volume per atom varies with the solute content. A change in lattice parameter requires either elastic distortions (a strain) or an array of dislocations (an interface) to accommodate the change of volume. Similarly, the presence of a curved interface between two different phases will alter the chemical composition of the two phases (§5.5.2). Despite these qualifications it is usually possible and useful to separate different microstructural changes on the basis of the principal component of the free energy driving the change.

In order to consider a particularly straightforward change in chemical free energy we can start with the solidification of a pure metal. Fig. 1.3 illustrates schematically how the free energy of a pure metal changes with temperature. At the melting point, T_m , the free energies of liquid and solid phases are equal. Below the melting point the solid has the lower free energy and is therefore the stable phase while above the melting point the reverse is true. The divergence of the free energy curves of the two phases as the temperature falls below the melting point produces a steadily increasing driving force for crystallisation of the supercooled liquid metal. The magnitude of the free energy change on crystallisation can be easily determined using this figure. Making the

simplifying assumption that the enthalpy and entropy changes of crystallisation, ΔH and ΔS , do not change significantly with temperature:

$$\Delta S = \Delta H / T_m \quad (1.8)$$

$$\Delta G = \Delta H(T_m - T) / T_m = \Delta H \Delta T / T_m \quad (1.9)$$

The assumptions, that ΔH and ΔS do not change with temperature, are valid if the specific heats of the two phases are the same, as shown, for example, by Gaskell (1983). The negative slope of either phase, $-dG/dT$ at constant pressure, is the *entropy* of that phase. The increase of entropy, ΔS , on melting leads to the *discontinuous* change of dG/dT at the melting point seen in fig. 1.3. The discontinuity in the *first differential* of G leads to Ehrenfest's descriptions of such equilibrium structural changes as being '*first-order*' transformations. The value of G itself changes continuously through the melting range. A few metallurgically important reactions, such as some, but not all, disordering transformations, involve a discontinuity in the second differential of G with respect to temperature and are thus '*second-order*' transformations.

The value of the latent heat of fusion, ΔH , for a typical metal such as copper is 13 kJ mole^{-1} , so the change of free energy of crystallisation will increase from zero at T_m (1356 K) to a maximum value of -13 kJ mole^{-1} as the temperature falls towards absolute zero (crystallisation of amorphous alloys at low temperatures is discussed in §3.4.4).

Solid state polymorphic changes such as that in iron at 1183 K and in tin at 291 K have lower heats of transformation: 0.9 and 2.2 kJ mole^{-1} , respectively. As a result the driving forces in solid state changes are smaller than those for solidification of the same metal at similar undercoolings. This difference is, however, offset to some extent by the larger undercoolings, ΔT , often encountered in solid state phase transformations. Jones and Chadwick (1971), using the standard methods of thermodynamics, have shown how the simple expression for the driving forces for crystallisation or solid state polymorphic changes is changed if the assumption of constant specific heat is relaxed. Due to compensating changes in the variation of both ΔH and ΔS with temperature, the effect of non-identical specific heats on the resulting ΔG values is usually rather insignificant, however.

Other examples of changes in chemical free energy are those occurring during diffusion in single-phase materials, for example, the homogenisation of 'cored' solid solutions, and in the precipitation of a second phase from a supersaturated solid solution. These changes can usually only be discussed semi-quantitatively since the exact forms of the relevant free energy–composition diagrams, see fig. 1.4, are not normally known. Approximate values of the free energy changes can be obtained by assuming, in the homogenisation case, that the solid solution is

1.2 Driving forces for microstructural change

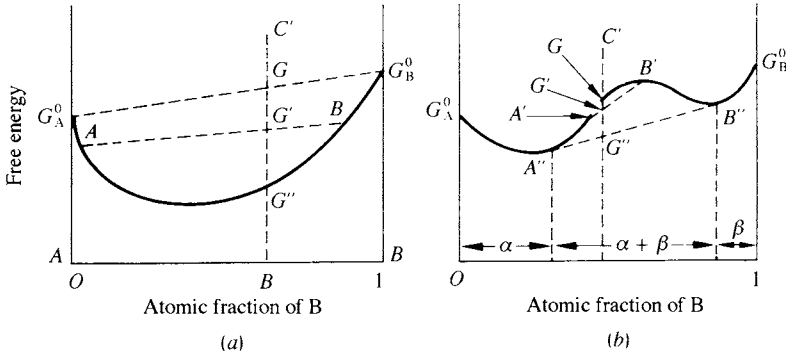


Figure 1.4 Free energy curves which lead to (a) homogeneous, (b) heterogeneous equilibrium.

ideal, and, for precipitation, that the activity coefficient of the solute remains constant in the composition range between the supersaturated solid solution and the equilibrium solubility. A constant activity coefficient is found for ‘dilute’ solutions but how dilute a solution must be for this to be valid is, again, not usually known.

For an ideal solid solution the free energy of mixing, ΔG_m , is given by:

$$\Delta G_m = -RT[(1 - N_B)\ln(1 - N_B) + N_B\ln N_B] \tag{1.10}$$

N_B is the atom fraction of component *B* in the binary solution. An extreme value of the change would be that achieved by the interdiffusion of two pure elements forming an equiatomic solid solution ($N_B=0.5$). The value of ΔG_m in these circumstances is $-0.7RT$. At 1000 K this energy change is $-5.7 \text{ kJ mole}^{-1}$. In the less extreme case of a cored solid solution, where the change of composition is less, a smaller value of driving force is found. For example, Doherty and Feest (1968) reported for cast copper–nickel ingots that the range of composition seen was from 48 to 77.5 wt% copper. An estimate of the free energy change on full homogenisation can be made by making the crude approximation that 50% of the alloy was at the average composition, 60% copper, 30% had the minimum composition and 20% had the maximum copper content. These assumptions yielded the result that the free energy change was $= -1.9 \text{ kJ mole}^{-1}$ at 1000 K.

The free energy changes associated with precipitation are illustrated in fig. 1.5. Here the α matrix at an alloy composition of N_0 (given as the atomic fraction of *B*) is supersaturated with respect to the equilibrium solubility N_α while the stable β phase has a composition N_β . The reduction of free energy on precipitation of the β phase is ΔG_1 per mole of *alloy*. However the reduction of free energy per mole of *precipitate* is the much larger value, $\Delta G_2=IJ$. This result is readily demonstrated using solution thermodynamics and fig. 1.5. To

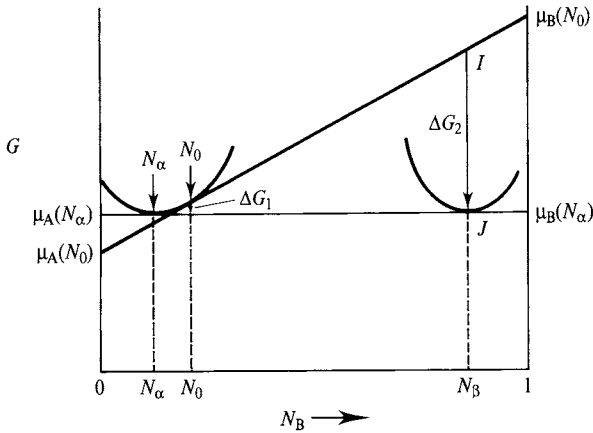


Figure 1.5 Free energy changes on precipitation from supersaturated solid solution.

make 1 mole of the β phase we must first remove N_β of a mole of B atoms and $(1 - N_\beta)$ of a mole of A atoms from the α phase. The B and A atoms have partial molar free energies, chemical potentials, of $\mu_B(N_0)$ and $\mu_A(N_0)$. One mole of such material, in the α phase but at the required composition of the β precipitate, has the free energy I in fig. 1.5. After transformation to the β phase, where the two components have the chemical potentials of $\mu_B(N_\alpha)$ and $\mu_A(N_\alpha)$, the free energy per mole of the precipitate is then J . That is, the change of free energy ΔG per mole of precipitate, ΔG_2 , is IJ . From the similar triangles, $N_\alpha - I - J$ and $N_\alpha - \mu_B(N_0) - \mu_B(N_\alpha)$, we can relate this value of ΔG_2 to the chemical potential change of the B component by eq. (1.11). (The geometry of this equation is not perfect but the errors introduced by the approximation are usually negligible.)

$$\Delta G_2 = J - I = [\mu_B(N_\alpha) - \mu_B(N_0)](N_\beta - N_\alpha)/(1 - N_\alpha) \quad (1.11)$$

The chemical potential of B is given by the activity, a_B , and thus by the product of the atomic fraction and activity coefficient, γ_B , of B atoms in the α phase, see eq. (1.12). μ_B° is the chemical potential of 1 mole of B atoms in the 'standard state' of B where the activity of B, a_B , is defined as $a_B = 1$. R is the gas constant, $8.31 \text{ J mole}^{-1} \text{ K}^{-1}$.

$$\begin{aligned} \mu_B(N_\alpha) &= \mu_B^\circ + RT \ln a_B = \mu_B^\circ + RT \ln(N_\alpha \gamma_B) \\ \mu_B(N_0) &= \mu_B^\circ + RT \ln a_B = \mu_B^\circ + RT \ln(N_0 \gamma_B) \end{aligned} \quad (1.12)$$

When the α matrix is a dilute solution, the usual case in most precipitation reactions, the activity coefficient, γ_B , is constant and so eq. (1.11) can be simplified to eq. (1.11a):